

LA-UR- 04-5860

Approved for public release;
distribution is unlimited.

Title: THERMOCHEMISTRY OF DEFECTS AND PHASE
STABILITY IN PuO_{2-x}

Author(s): Marius Stan, Petrica Cristea, and Terry C. Wallace, Sr.
MST-8

Submitted to: 11th Symposium on Thermodynamics of
Nuclear Materials
Karlsruhe, Germany
Sept. 6-10, 2004.



Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.



Form 836 (8/00)

STNM-11

11th Symposium on Thermodynamics of Nuclear Materials
Karlsruhe, Germany, Sept. 6-10, 2004.

M. Stan, P. Cristea, and T. C. Wallace Sr.,
Los Alamos National Laboratory

Defect Thermochemistry and Phase Stability in PuO_{2-x}

ABSTRACT: Based on a thermochemical model of defect formation, the concentration of various types of defects and the non-stoichiometry of PuO_{2-x} are calculated as functions of temperature and partial pressure of oxygen. The model is able to predict oxygen diffusivity for temperatures in the (900, 1400) °C range and oxygen pressure ($1, 10^{-25}$) atm. Comparison with experimental data shows that the model describes non-stoichiometry and oxygen diffusivity well. The calculated free energy of non-stoichiometric plutonia is used to derive the high oxygen, high temperature, region of the Pu-O phase diagram, which is still subject of controversy. The thermochemistry of PuO_{2+x} , if any, is also discussed.

STNM-11
11th Symposium on Thermodynamics of Nuclear Materials
Karlsruhe, Germany, Sept. 6-10, 2004

**Thermochemistry of Defects and
Oxygen Diffusion in PuO_{2-x}**

M. Stan*, P. Cristea, and T. C. Wallace Sr.,

**Los Alamos National Laboratory
Materials Science and Technology Division
Los Alamos, NM 87545**

***mastan@lanl.gov**

Contributors and collaborators (LANL) :

**P. Cristea, T. C. Wallace, Sr., S. M. Valone, K. O. Pasamehmetoglu,
K. J. McClellan, and S. L. Voit.**

UNCLASSIFIED

LA-UR-04-4197



ABSTRACT

Thermochemical models of PuO_{2-x} are necessary for prediction of oxidation-reduction of Pu-based alloys and for the design of better oxide nuclear fuels. The type and defect formation mechanism determine the alloy performance while kinetic properties of point defects govern radiation tolerance and fission gas release. Oxygen diffusion is also important in optimizing surface properties. Together with the phase stability, diffusion governs the non-stoichiometry of the alloy. Modeling the defects and the mobility of oxygen opens a path to the modeling of the more complex phenomena, such as ageing. Although the Ce-O and Pu-O phase diagrams are still controversial in the high temperature region, there is a consensus regarding the existence of fluorite (f.c.c.) phases in the region $x < 0.3$ and $1000 < T < 2000$ K.

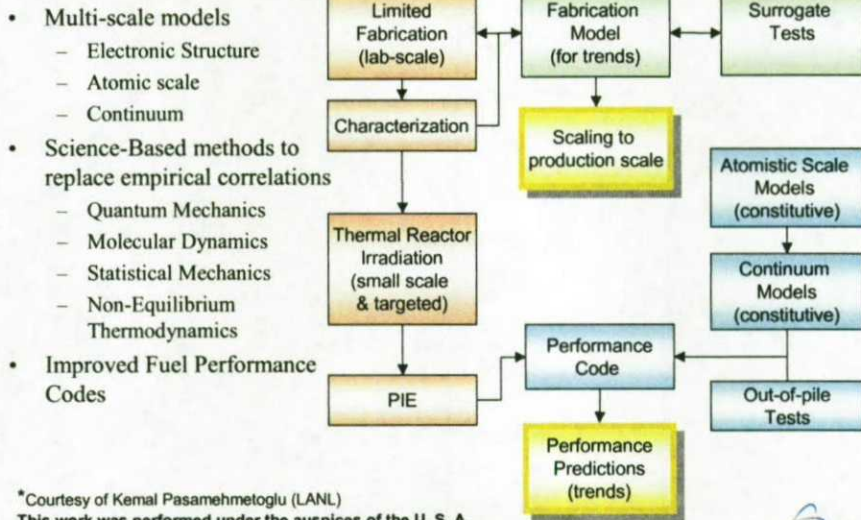
A thermochemical model of defect formation in CeO_{2-x} and PuO_{2-x} was developed and implemented in a computer program able to predict the concentration of various types of defects and the non-stoichiometry as functions of temperature and partial pressure of oxygen. The model is based on five types of defects: polarons, singly and doubly-charged oxygen vacancies, singly-charged metal-oxygen vacancy complexes, and neutral oxygen vacancy complexes. The same program was used to calculate the oxygen chemical and self-diffusivity in CeO_{2-x} and PuO_{2-x} for temperatures of (1200, 1700) K and oxygen pressures ($1, 10^{-25}$) atm. The model is currently used to determine the oxygen chemical potential as a function of oxygen partial pressure and temperature, as part of a new calculation of the Ce-O and Pu-O phase diagrams. The approach will be extended to UO_{2+x} , taking into account the specific defect types.

UNCLASSIFIED

LA-UR-04-4197



The role of Models and Simulations in Advance Fuel Cycle Initiative (AFCI)*

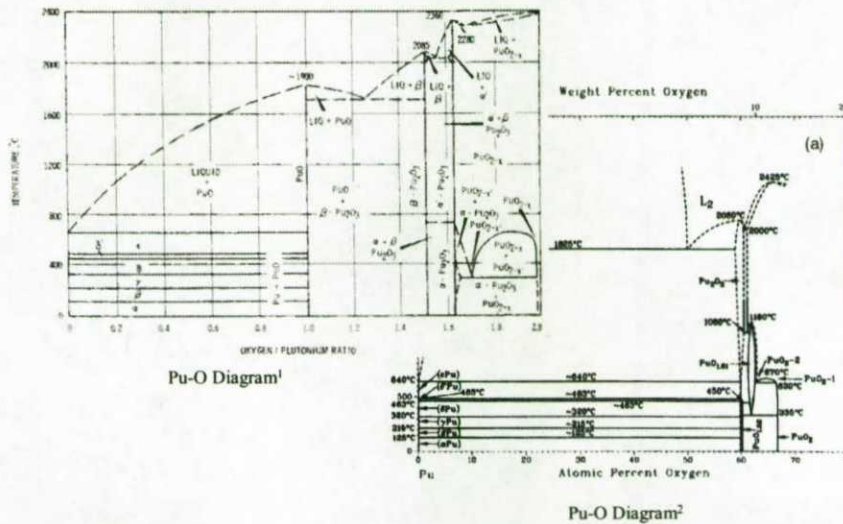


*Courtesy of Kemal Pasamehmetoglu (LANL)

This work was performed under the auspices of the U. S. A. Department of Energy, the Advance Fuel Cycle Initiative program.



Pu-O Diagram is uncertain

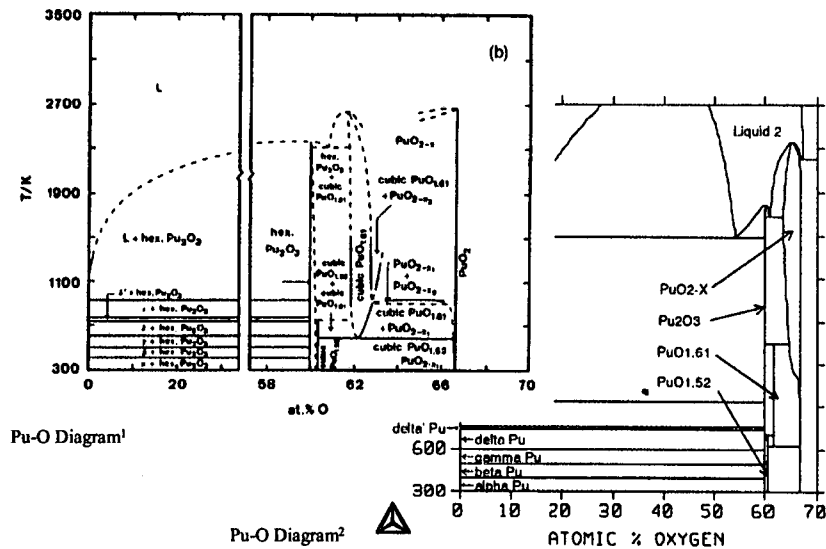


¹T. D. Chikalla, C. E. McNeilly, and R. E. Skavdahl, J. Nucl. Mater., 12 (1964) 131-141.

²H. A. Wriedt, Bulletin of Alloy Phase Diagrams, 11 (1990) 184-202



Pu-O Diagram is uncertain (cont.)

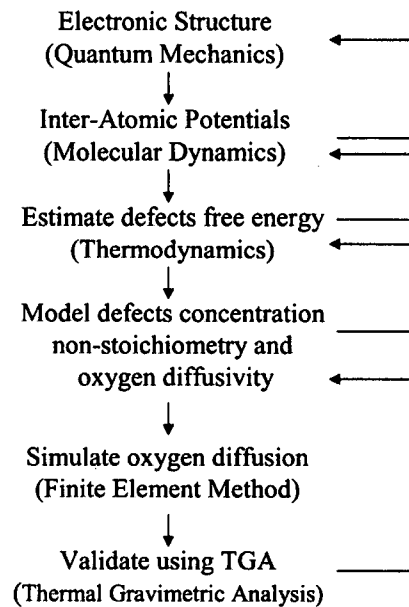


¹E.H.P. Cordfunke and R.J.M. Konings, *In Thermochemical Data for Reactor Materials and Fission Products*, North-Holland, Amsterdam, 1993.
²H. Kinoshita, M. Uno, and S. Yamazaki, *J. Alloys Compd.*, 354 (2003) 129-137.

Los Alamos
NATIONAL LABORATORY
EST. 1943

A new approach

- Multi-Scale Models and Simulations.
- All types of defects must be taken into account.
- Homogeneous, isotropic properties, for now.



Los Alamos
NATIONAL LABORATORY
EST. 1943

Defect Thermodynamics

$$G_{\text{Defective crystal}} = G_{\text{Perfect crystal}} + \Delta G$$

$$\Delta G = \Delta G_{\text{Formation}} - T\Delta S_{\text{Configurational}}$$

$$\sum_i N_i \langle g_{SR,i} \rangle \leftarrow \Delta G_{F,SR}^{\text{Short-range}} + \Delta G_{F,LR}^{\text{Long-range}} - T k_B \ln \Omega$$

\downarrow Function of defect concentration via N_i (number of i -type defects)
 \downarrow $\langle g_{SR,i} \rangle$ Independent of defect concentration
 \downarrow Function of defect concentration (long-range, i.e. coulombic interaction)
 \downarrow Function of defect concentration

$G \equiv$ Gibbs free energy

$\Omega \equiv$ the number of ways of arranging all defects in a lattice with given symmetry = $\prod_i \Omega_i$

$k_B \equiv$ Boltzmann constant



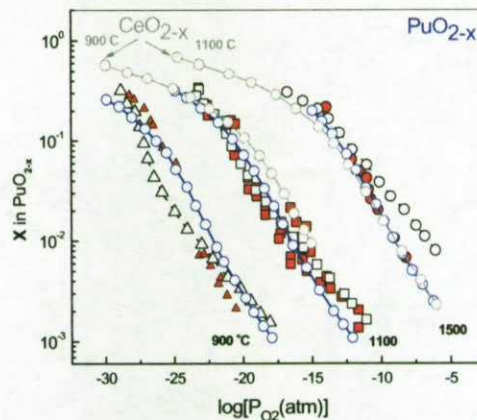
CeO_{2-x} as a Surrogate for PuO_{2-x}

Blue circles – calculated (this work);

black open triangles, squares, and circles – calculated [1];

red triangles, squares and circles – experimental [2-6]

- Same fluorite structure.
- Similar defect types.
- Similar Gibbs free energy of the fluorite phase.
- Similar free energy of formation.
- Similar temperature and concentration intervals of stability.



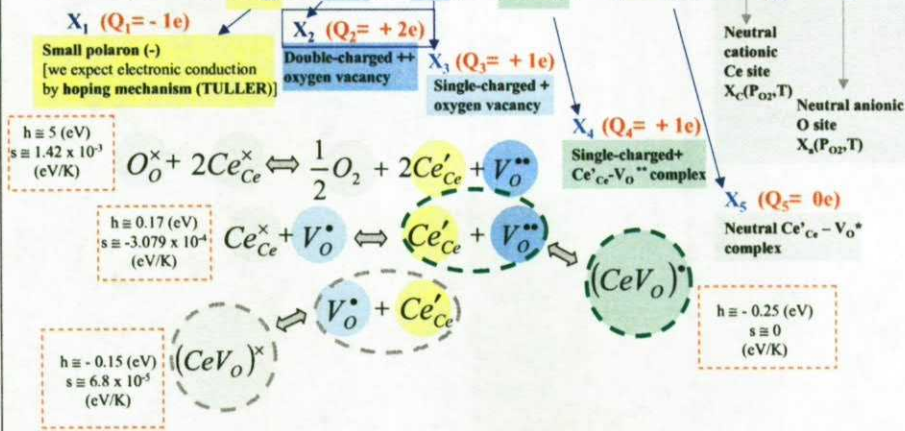
[1] A. Nakamura, J. Nucl. Mater., 201 (1993) 17-26. [2] T. L. Markin and M. H. Rand, Thermodynamics; Proc. IAEA, Vienna, Vol. I, 1966, pp. 145. [3] G. C. Swanson, Los Alamos National Laboratory Report (LA-6063-T), 1975. [4] L. M. Atlas and G. J. Schleman, Proc. IAEA, Vienna, Vol. II, 1966, pp. 407. [5] O. T. Sorensen, in Plutonium 1975 and other actinides, North-Holland Pub. Co., Amsterdam, 1976, p. 123. [6] R. E. Woodley, J. Nucl. Mater., 96 (1981) 5-14.



Defect Interactions in CeO_{2-x} ¹

DEFECTS (Kroger-Vink notation²)

Subscript assignments: 1- Ce'_{Ce} ; 2- VO^{**} ; 3- VO^* ; 4- $(\text{CeVo})^*$; 5- $(\text{CeVo})^x$; 6- Ce^x_{Ce} 7- O^x_{O}

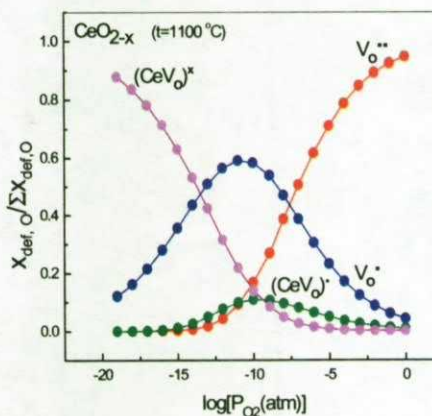


¹S. Ling, Phys. Rev. B 49 (1994) 864.

²F. A. Kröger and H. J. Vink, in Solid State Physics: Advances in Research and Applications, edited by F. Seitz and D. Turnbull (Academic, New York, 1956) 3, 307.

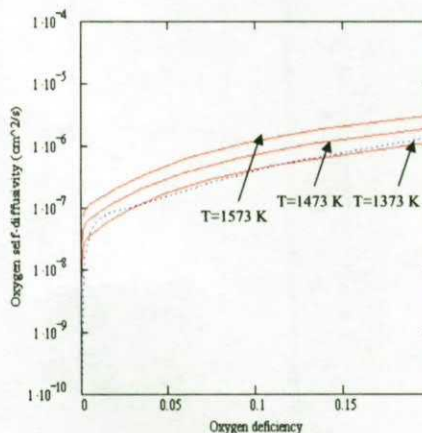
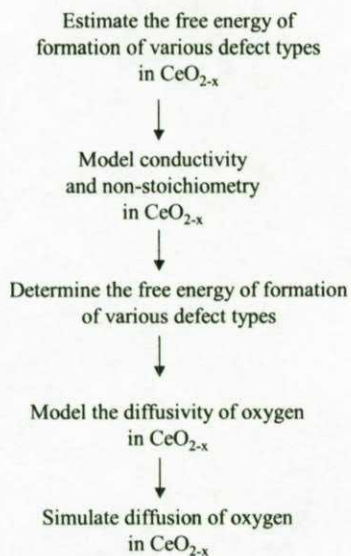
Relative Contribution of Oxygen Defects in CeO_{2-x} ¹

- Relatively high partial pressure, low defect concentrations, close to CeO_2
 - Oxygen vacancies
- Low partial pressure, high defect concentration
 - Neutral complex



¹P. Cristea and M. Stan, submitted to Phys. Rev. B., 2004.

Oxygen Diffusivity in CeO_{2-x}



Calculated oxygen self-diffusivity in CeO_{2-x} as a function of non-stoichiometry (x) and temperature (red) and comparison with experimental data¹ (blue).

¹B. C. H. Steele and J. M. Floyd, Pr. Br. Ceram. Soc. **19** (1971) 55-71.



TGA Model Assumptions

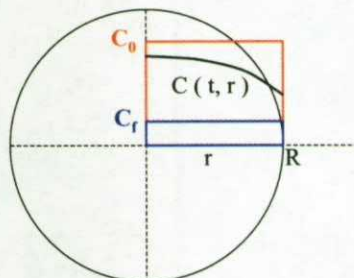
- (1) The oxygen is uniformly distributed in the sphere at the initial time ($t = 0$).
- (2) All spheres are of same radius, R .
- (3) The radius does not change during the diffusion process.
- (4) The rate of mass exchange is proportional to the difference between the final concentration of the environment (C_f) and the concentration at the surface of the sphere (C_s):

$$\frac{dM}{dt} = \alpha(C_f - C_s)$$

where M is the amount of diffused substance per unit area.

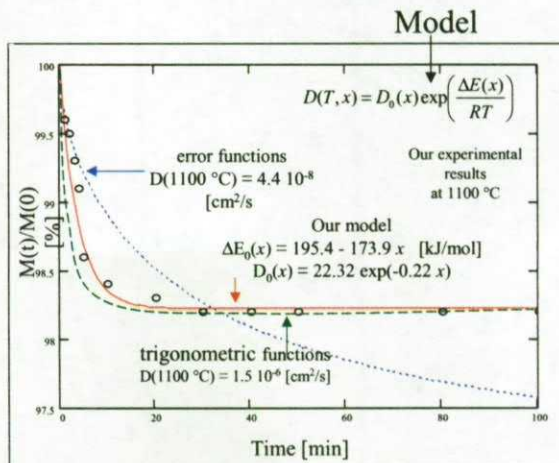
$C_0 = 18.6\text{ wt.}\%$ (phase diagram, $1100\text{ }^\circ\text{C}$)

$C_f = 16.8\text{ wt.}\%$ (TGA, $1100\text{ }^\circ\text{C}$)



Oxygen Diffusion in CeO_{2-x} ¹

- Error functions describe well diffusion at short times.
- Trigonometric functions describe well diffusion at long times.
- Our model reproduces well the TGA results in the entire time interval

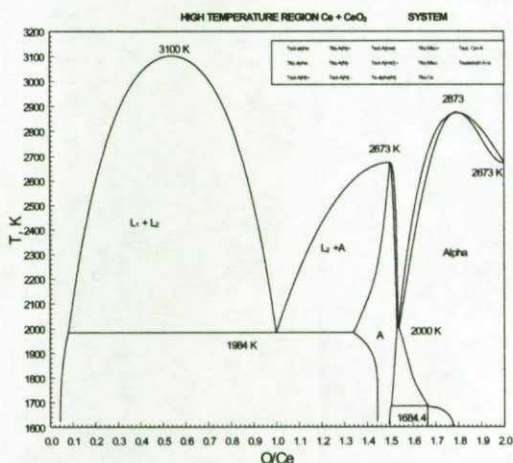


¹M. Stan, Y. T. Zhu, H. Jiang, and D. P. Butt, J. Appl. Phys., **95** (2004) 3358-61.



Calculated High Temperature Ce-O Phase Diagram¹

- Phase diagram under development.
- Two methods combined:
 - Temperature integration of oxygen partial pressure experimental data
 - Calculation of free energy from defects
- Lack of experimental data at high temperatures.

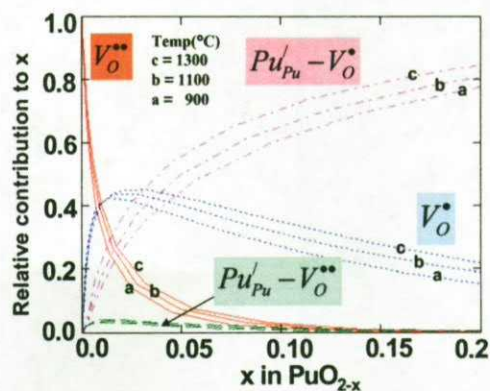


¹M. Stan, T. C. Wallace, Sr., and P. Cristea, in preparation for J. Amer. Ceram. Soc., 2004.



Relative Contribution of Oxygen Defects in PuO_{2-x} ¹

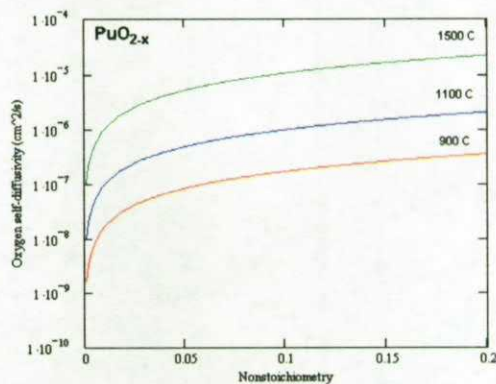
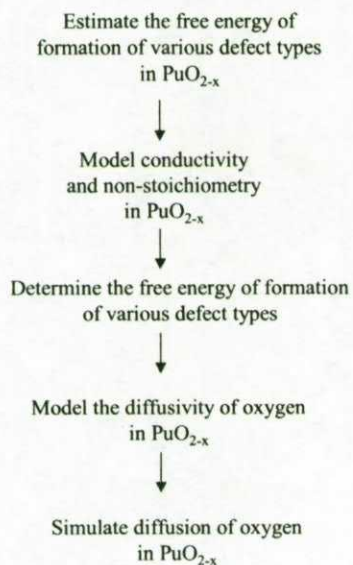
- Low defect concentrations, close to CeO_2
 - doubly charged oxygen vacancies
- Intermediate defect concentration.
 - singly charged oxygen vacancies
- High defect concentration
 - Neutral complexes: polaron + singly charged oxygen vacancy
- Defect concentration increases with temperature.



¹M. Stan and P. Cristea, submitted to J. Nucl. Mater., 2004.



Oxygen Diffusivity in PuO_{2-x}



Calculated oxygen self-diffusivity in PuO_{2-x} as a function of non-stoichiometry (x) and temperature.



Free Energy of PuO_{2-x}

Excess Gibbs free energy due to defects

$$\Delta G^{ex}(T, x)$$

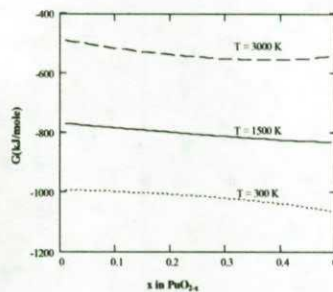
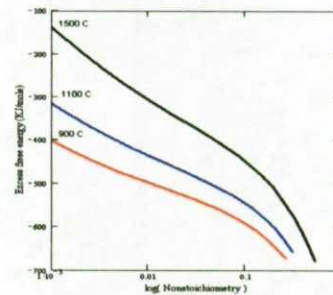
Gibbs free energy of formation of PuO_{2-x}

$$\Delta G_{\text{PuO}_{2-x}}^f(T, x) = \Delta G_{\text{PuO}_2}^f(T) + \Delta G^{ex}(T, x)$$

Gibbs free energy of PuO_{2-x}

$$G_{\text{PuO}_{2-x}}(T, x) = \Delta G_{\text{PuO}_{2-x}}^f(T, x) + \frac{2-x}{2} G_{\text{O}_2}(T) + G_{\text{Pu}}(T)$$

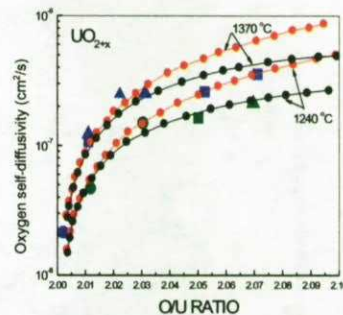
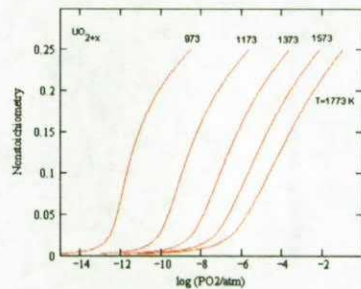
Pu-O phase diagram



Los Alamos
NATIONAL LABORATORY
EST. 1947

Extension to UO_{2+x}

- Results using the MO_{2-x} formalisms are wrong and misleading.
- New types of defects must be included
 - U vacancies
 - O interstitials
 - New complexes
- A new model is in progress.



Los Alamos
NATIONAL LABORATORY
EST. 1947

CONCLUSIONS

- The type and defect formation mechanism determine the alloy performance .
- A thermochemical model of defect formation in CeO_{2-x} and PuO_{2-x} was developed and implemented in a computer program able to predict the concentration of various types of defects and the non-stoichiometry as functions of temperature and partial pressure of oxygen.
- The model is based on five types of defects: polarons, singly and doubly-charged oxygen vacancies, singly-charged Pu-oxygen vacancy complexes, and neutral oxygen vacancy complexes.
- The same program was used to calculate the oxygen chemical and self-diffusivity in CeO_{2-x} and PuO_{2-x} for temperatures of (1200, 1700) K and oxygen pressures ($1, 10^{-25}$) atm.
- The model is currently used to determine the oxygen chemical potential as a function of oxygen partial pressure and temperature, as part of a new calculation of the Ce-O and Pu-O phase diagrams.
- The approach will be extended to UO_{2+x} , using a different set of defect types.